Alternative methods for analysing moisture transport in buildings
Utilisation of tracer gas and natural stable isotopes

by
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Stockholm 2003
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Doctoral Thesis
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May 2003

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ISSN 1651-5536
ISRN KTH-BYT/R—03/191-SE
The figure on the cover page shows *Clarkia Pulchella*, named in honour of the American frontiersman William Clark. The fertilization process of the flower was studied by Robert Brown, who recognized, in contrast to both predecessors and contemporaries, that the rapid oscillating movements of the pollen grains were not of organic character as could be verified through examinations of particles of glass and other inorganic material. It was later shown that molecules behave similarly and that the diffusion mechanism can be seen as a macroscopic manifestation of their continuous thermal motion.
ABSTRACT

New methods, based on tracer gas measurements and isotopic analysis can be used to evaluate the moisture properties of building materials and provide the means for forensic analysis of the origins and history of excessive water in buildings, the immediate practical consequences of which will be the ability to improve the moisture performance of constructions.

It is shown, in theory and through measurements how the water vapour permeability of porous building materials can with a good degree of accuracy be estimated with tracer gas measurements that provide an efficient alternative to the cup method. Complementary measurements may be carried out in order to evaluate the contribution of surface diffusion and the eventual enhancing effects of moisture content on the diffusion coefficient. The Random Hopping Model is used to illustrate how the surface diffusion coefficient depends on the amount adsorbed and the activation energy of migration that can be evaluated from the sorption isotherms.

It is explained how the abundance ratios of two of the most ordinary isotopes of hydrogen and oxygen in water can be used to determine its history. These isotopes are stable and give the water a distinct signature that can be used to reveal its source as shown in a case study. In a contrary manner the measured isotopic separation can be used to determine the relevance of different transport processes and reactions. It is of central importance that not only does the magnitude of isotopic separation for the reactions vary for deuterium and oxygen-18 but even the ratio thereof. One of the challenges has been to construct an experimental method for retrieving samples of water for comparison.

Furthermore this thesis includes an evaluation of a new type of a light weight construction with loose-fill cellulose fibre, in which the conventional polyethylene vapour barrier has been replaced with polypropylene fabric. With a verified model it has been investigated how the construction would perform for different internal moisture loads and reference climate from the literature. The results suggest that this type of construction is not to be recommended.
KEYWORDS: tracer gas, water vapour permeability, diffusion, surface diffusion, isotopic analysis, deuterium, oxygen-18, fractionation, vapour barrier, transient numerical modelling of diffusion.
PREFACE

This doctoral thesis is the result of my research during the past six years at the Division of Building Technology at Kungliga Tekniska Höskolan in Stockholm, Sweden. The project has mainly been financed by the Swedish Council for Building Research (BFR) and then FORMAS to whom the author wants to express his gratitude.

The work started with a project the concern of which was to evaluate the moisture properties of a light weight construction in which the traditional vapour barrier had been omitted in favour of a polypropylene fabric. This study included both measurements and modelling that was carried out in order to estimate how the construction would behave under different conditions.

While carrying out the modelling it became obvious that it would be of value to develop a method for estimating the water vapour permeability of porous building materials in an efficient manner. Of special interest was to investigate whether this could be done with dinitrogen oxide as a tracer gas and standard equipment used to measure the air exchange in buildings.

In order to do this it was necessary to illuminate the physical mechanisms that are involved in the transport of moisture in building materials. This investigation was rewarding, not at least due to the extraordinary contribution of the late Feras Abbas. It had however soon become evident that complementary measurements of surface diffusion may sometimes be required in order to measure the familiar concentration dependency of the water vapour permeability.

The more theoretical work of the tracer gas study is also a vital component of another subject of this project, in which it has been investigated how the isotopic fingerprints of water can be used to reveal its history and origin. The inspiration came from another field of research, namely that of hydrogeology, in particular the scientists at the Division of
Geophysics at the Science Institute of the University of Iceland to whom gratitude is in order, especially Árny Erla Sveinbjörnsdóttir, who is the head of the Division.

I would like to thank all my colleagues at the department at KTH. Special thanks are due to associate Professors Folke Björk and Per Levin, the co-author of the first article, for their advice and helpfulness. I am also grateful to the supervisor, Professor Gudni Jóhannesson at the Division of Building Technology for a long list of reasons, including support, guidance and encouragement.

During the year of 1998 I spent some six months at the ETH in Zürich, Switzerland. I would like to thank Professor Bruno Keller and the colleagues at the Chair for Building Physics for their help on the subject and how to approach it. The stay in Switzerland was made possible by a scholarship from “Stockholms Byggnadsförening” to whom the author is grateful.

Stockholm
May 2003

Kjartan Gudmundsson
LIST OF PAPERS

I. Moisture in Constructions with Loose-Fill Insulation and no Vapour Barrier
Per Levin and Kjartan Gudmundsson
Published in Nordic Journal of Building Physics

II. An approach to determining the water vapour transport properties of building materials
Kjartan Gudmundsson
Submitted to Nordic Journal of Building Physics

III. Isotopic tracing of moisture in buildings
Kjartan Gudmundsson
Published in Nordic Journal of Building Physics

IV. Tracer gas measurements of water vapour permeability of porous building materials
Kjartan Gudmundsson
Submitted to Building and Environment

V. Forensic analysis of moisture transport in building materials with natural stable isotopes
Kjartan Gudmundsson
Submitted to Building and Environment
# TABLE OF CONTENTS

1. Introduction ...................................................................................................................... 1

   1.1 Moisture in constructions with loose-fill insulation and no vapour barrier ...... 3

   1.2 Tracer gas estimations of the water vapour permeability ................................. 4

   1.3 Isotopic analysis of the origins of water in buildings ....................................... 5

   1.4 Isotopic analysis of moisture transport and reactions ..................................... 6

2. Scope .................................................................................................................................. 6

3. Historical background ...................................................................................................... 11

   3.1 Diffusion .................................................................................................................. 11

   3.2 Isotopes .................................................................................................................. 13

4. Methodology ..................................................................................................................... 15

   4.1 Moisture in constructions with loose-fill insulation and no vapour barrier ...... 15

       Measurements ........................................................................................................... 15

       Calculation model ................................................................................................... 16

   4.2 Tracer gas measurements..................................................................................... 17

       Ordinary diffusion ................................................................................................... 18

       Knudsen diffusion ................................................................................................... 19

       Combined transport and the DGM material parameters .................................... 20

       Measurements of the water vapour permeability with N\textsubscript{2}O .................. 22

       Surface diffusion .................................................................................................... 23

   4.3 Isotopic analysis ....................................................................................................... 27

       Definitions ............................................................................................................... 27

       Meteoric line .......................................................................................................... 29

       Rayleigh processes ............................................................................................... 30

       Experimental procedure ....................................................................................... 30

       Isotopic analysis of excessive water .................................................................. 31
Isotopic analysis of reactions ................................................................. 32
Adsorption and capillarity ................................................................. 34
Diffusion experiment ......................................................................... 35

5. Results .............................................................................................................. 37
   5.1 Measurement results for construction with no vapour barrier ............ 37
   5.2 Calculation model for construction with no vapour barrier ................. 38
   5.3 Simulation for construction with no vapour barrier .............................. 40
   5.4 Tracer gas measurements ................................................................. 43
   5.5 Sorption measurements .................................................................... 45
   5.6 Activation energy and surface diffusion ............................................. 46
   5.7 Isotopic analysis of excessive water .................................................... 47
   5.8 Reactions and isotopic differences .................................................... 50

6. Practical consequences .................................................................................. 51
   6.1 A moisture barrier is needed ............................................................. 51
   6.2 Evaluation of material properties regarding moisture transport .......... 51
   6.3 Identification of excessive water ......................................................... 52
   6.4 Analysis of transport processes and reactions with isotopes ............... 52

References ......................................................................................................... 54

Paper I. Moisture in Constructions with Loose-Fill Insulation and no Vapour Barrier

Paper II. An approach to determining the water vapour transport properties of building materials

Paper III. Isotopic tracing of moisture in buildings

Paper IV. Tracer gas measurements of water vapour permeability of porous building materials

Paper V. Forensic analysis of moisture transport in building materials with natural stable isotopes
1. INTRODUCTION

Tracer gas measurements and isotopic analysis are methods that can be used to evaluate the material parameters that control moisture transport and to illuminate the role of the different transport mechanisms in the flow of water and water vapour. Needless to say this can be of benefit when modelling the moisture performance of constructions and therefore of value in the defence against one of the most destructive elements of nature.

A standard method for obtaining the water vapour permeability is to use the cup method. In brief, the material to be tested is placed on top of a cup, while ensuring that the joint between the specimen and the cup is tight and that the edges of the specimen are sealed. The measurements are normally carried out with a wet cup that contains water and a salt solution with a relative humidity that exceeds that of the environment and also a dry cup with a relative humidity that is lower than that of the surroundings. The weight loss of the wet cup is registered as well as the weight gain of a dry cup in the same environment. When the rate of change in the weight of the cups has reached a steady state the water vapour permeability can be calculated. This method is time consuming and requires a climatic chamber in order to keep the background concentration at a constant level. Therefore it has been of great interest to investigate what information about the water vapour permeability can be obtained from measurements of the tracer gas permeability of a material with dinitrogen oxide. These efforts are revised in this dissertation and it is shown how the contribution of Fickian diffusion to the transport of water vapour can be estimated with tracer gas measurements. Some complementary measurements with water vapour may be required, however, when the material has a diffusion coefficient that increases strongly with the moisture content since this enhancing effect that can be ascribed to the contribution of surface diffusion is dependant of the gas-surface interaction between the water vapour and the porous material. The accuracy required of material data must on the other hand depend on the moisture properties of the other materials in the construction as well as the placement of the material in the construction (Geving, 1997).
This thesis does also propose a new method for analysing the origins of excessive moisture in buildings by isotopic analysis. It is described how the isotopic content of a water sample can be used to determine its origins and how the effects of reactions on the isotopic content can be counted for. Included is also a description of how changes in the
isotopic content might be used to determine which physical processes a sample has undergone.

Furthermore this thesis includes an evaluation of a new type of a light weight construction with loose-fill cellulose fibre, in which the conventional polyethylene vapour barrier has been replaced with armoured polypropylene fabric. With a model that was verified through measurements it was investigated how the construction would perform under a internal moisture load, i.e. a difference in vapour content due to moisture production inside a building, corresponding to 2 g/m$^3$ and 4 g/m$^3$ using a reference climate from the literature.

Figure 1 shows the framework of the thesis and the relationship between the subjects of study. A more thorough description of the main topics of this thesis is given in the following text.

1.1 Moisture in constructions with loose-fill insulation and no vapour barrier
The effects of replacing the traditional polyethylene vapour barrier in a lightweight construction have been investigated with in-situ measurements of the moisture content and temperature in the walls, roofs and floors of three houses as well as simulations that predict the moisture performance for more severe moisture production and a given reference climate from the literature.

The measurements of moisture content and temperature in the outermost part of the insulation of the constructions were carried out every three weeks over a two-year period, during which the indoor temperature and relative humidity were continuously registered. Based on the actual indoor climate and information from a nearby weather station, the moisture conditions have also been calculated using a one-dimensional transient diffusion model that takes into account the sorption properties of the materials.

The results of the measurements show that for the low moisture loads in the three houses there is no immediate risk of moisture damage.
The results of the simulations show good correlation with measurements and therefore the model was used to simulate the conditions for a design moisture load of 2 and 4 g/m$^3$. The results indicate that even for the lower design load moisture would accumulate and condense in the wall construction. As high relative humidity would for long periods of time coincide with temperatures feasible for mould growth, the wall construction is not to be recommended.

A similar simulation of the piled floor construction shows that even for moderate moisture loads the risk for condensation is high. A correlation for the roof construction could not be achieved without adjusting parameters and therefore the model was not considered valid for the roof.

### 1.2 Tracer gas estimations of the water vapour permeability

In the lower hygroscopic region the transport of water vapour is mainly due to ordinary diffusion and to some extent through Knudsen diffusion for materials with relatively many small pores but in both cases the flow rate of diffusion increases linearly with the

![Figure 2](image.png)

Figure 2: The setup of the tracer gas measurements. Further description is to be found in paper IV.
concentration gradient according to Fick’s law of diffusion (Crank, 1975). In addition some porous materials exhibit an enhancing effect of concentration on the water vapour permeability that can be explained by the contribution of surface diffusion.

The potential contribution of Fickian diffusion can to a good degree of accuracy be evaluated with tracer gas measurements using dinitrogen oxide in a simple and efficient manner.

When of relevance, the contribution of surface diffusion must however be evaluated with complementary water vapour measurements since it is related to interaction between the gas and the inner surface of the porous material. The surface diffusion coefficient depends on the rate of jumping, which in turn depends on the amount adsorbed and the activation energy needed to trigger a jump as described by the Random Hopping Model. The activation energy can be evaluated by measuring the sorption isotherms of a material.

1.3 Isotopic analysis of the origins of water in buildings

The isotopic composition of water can be used to determine its origins. For the building industry this provides a new method for investigating the sources of excessive water in buildings. The method is based on measurements of the abundance ratio of two of the most ordinary isotopes of hydrogen and oxygen, which by definition is the ratio of the heavier to the light isotope, that is the ratio of D to H and the ratio of oxygen-18 to oxygen-16. These isotopes are to be found in all water and since they are stable, in the sense that they do not disintegrate with time, they give every sample of water a distinct signature that can be used to reveal its source. The abundance ratios change, however, as water undergoes reactions, such as diffusion, condensation or evaporation and the use of isotopic fingerprints as a means to determine the origins of leakage requires that the effects of these reactions are taken into account.

Isotopic analysis has previously been used in the field of hydrogeology to trace the provenance and flow of groundwater as well as to monitor the recharge processes, the subsurface processes and the geochemical reactions. It has also proved useful in climatic
research where the known dependency of isotopic content on temperature has been used to study the climatic changes by isotopic measurements of ice cores from the Greenland glacier (Dansgaard et al., 1993).

1.4 Isotopic analysis of moisture transport and reactions
When the reactions involved in moisture transport are known it is possible to use the isotopic signature to trace the origins of water. In a contrary manner the measured isotopic separation can be used to determine the relevance of different transport processes and reactions when the source of water is known. It is of central significance that not only does the magnitude of isotopic enrichment or depletion vary for the different reactions but also the ratio of the isotopic difference of deuterium over that of oxygen-18.

One of the challenges of deriving the reactions that are involved in moisture transport from the isotopic separation is to construct an experiment, the effects of which on the isotopic content are none or that can be calculated and taken into account. As suggested in this study the problem can sometimes be bypassed by evaluating the effects of reactions through measurements of the isotopic content of the remaining water. In the case of sorption and capillary uptake the material and the interacting surroundings are supposed to be a closed system with a constant mass of water, while the effects of diffusion are derived from the isotopic content of the remaining water under the assumption that the isotopic difference increases exponentially as the reservoir vanishes.

2. SCOPE
In this section the boundaries of this work are described and references are given to some of the complementary work within the field of building physics. A brief description of the historical development behind the theories that are applied is however to be found in the following chapter while references to the most closely related current work is given in each section and the respective papers.

In the assessment of the wall and roof construction with no vapour barrier the purpose was to investigate whether there was a risk for condensation in the construction for a given design load and climatic conditions. It was assumed that all flows are purely
diffusive but a more thorough study of the moisture distribution when condensation occurs would have to include the effects of capillary transport within the material.

This thesis does also contain the results of a project the aim of which was to investigate how tracer gas measurements can be used to evaluate the water vapour permeability of porous building materials. Of primary interest was to develop a method to obtain the information normally obtained from “cup method” measurements but in a faster and more economic manner. The efforts were focused on identifying the most significant transport processes in porous material with moisture content below the critical moisture content and establishing a connection between the transport of water vapour and tracer gas through a porous material. This could be done with the help of the Dusty Gas Model since it provides a formulation of the relevant transport processes as explicit functions of the thermodynamic properties of gases and the textural properties of the material as well as the means to combine the contributions of the different flow mechanisms. It was, on the other hand, well beyond the purpose of this study to give a thorough treatment of the molecular dynamics of gases and how they relate to the thermodynamic properties.

In the present study it is assumed that the transport processes of ordinary diffusion and Knudsen diffusion are connected in series while their contribution to the total flow can be measured independently and added to that of surface diffusion. The contribution of viscous gas flow can also be added to the contributions of the other mechanisms although that transport process will seldom be relevant when it comes to building materials (and then perhaps only when accounting for pressure gradient in laboratory experiments). This approximation is based on previous experimental work from the field of physical chemistry (Mason and Malinauskas, 1983; Tuchlenski et al., 1998), even though it should be noted that there is known to be a coupling effect between viscous flow and ordinary diffusion as well as between viscous flow and Knudsen diffusion, i.e. diffusive slip and viscous slip.

The contribution of surface diffusion is of great interest since it can be used to explain the inconstancy in results from wet- and dry-cup measurements, i.e. the enhancing effects of
concentration on the water vapour permeability. By using the Random Hopping Model, surface diffusion can be modelled as the jumping of molecule between sorption sites, where the diffusion coefficient must depend on the time between the jumps that can be related to the amount adsorbed and the activation energies that are needed to trigger a jump. It is shown how the activation energies can be obtained from the sorption isotherms under the assumptions of the Brunauer-Emmett-Teller (BET) theory for sorption.

It has, however, been beyond the scope of this work to investigate the BET-model thoroughly and to do a comparative study of other sorption models.

The combined flow of heat and moisture are not the topic of this study. One well known model of the phenomena is that of Philip and de Vries a brief account of which is given in a paper by de Vries (1987). According to de Vries, and notable in the context of this thesis is that the phenomena of surface flow as well as Knudsen diffusion is not taken into account in the model and that the pressure is assumed to be uniform and constant.

The research of de Vries dates back to the 1950s as does the related and commonly referred to work of Lykow (1958) on transport in porous material. An account of both and related work from the same period is given in the publication of Lund-Hansen (1967) on moisture transport in building materials. Lund-Hansen describes fixation and transport in porous material including a review of sorption curves and their measurements as well as the relationship between the capillary potential or suction to the partial vapour pressure and how they relate to the moisture content. The transport mechanisms in both vapour and liquid phase are mentioned including Fickian diffusion, Knudsen diffusion, surface diffusion and capillary flow. Lund-Hansen points out that for practical purposes the total transport is conveniently modelled as the sum of Fickian diffusion contribution, driven by the gradient of partial pressure and governed by the water vapour permeability of the material, and the capillary flow where the moisture content is the potential and the flow rate is controlled by the capillary conductivity of the material. The author describes measurements of both material properties as well as the simultaneous measurements of
heat and moisture and states that water vapour permeability of hygroscopic materials increases with the relative humidity.

The topic of coupled heat and moisture transport in building materials was later investigated by Andersson (1985), who discusses the relevance of various terms in a set of equations for combined heat and moisture transport, where the potentials are the pore water pressure and the partial vapour pressure, whereas de Vries used the moisture content and the temperature. Andersson takes into account the inducing effects of heat flow due to the effect of temperature on the state of moisture as well as the effect of temperature through condensation and evaporation, through the transport of heat with vapour and water and the effect on the moisture transfer coefficients. One of the conclusions that the author draws from a calculated example for aerated concrete is that large temperature fluctuations will have a considerable effect on the flow of water in vapour phase while the flow of water vapour will have negligible effect on the transport of heat. The study is concerned with moisture transport both under and above the critical moisture content, i.e. flow in vapour phase and capillary flow respectively.

Later work includes the contribution of Krus (1995), which investigated the fixation and transport of water vapour in both the hygroscopic and capillary region, with emphasis on the latter. It is described how the relationship between suction and moisture content can preferably be derived from pressure plate measurements and how the results can be combined with the hygroscopic sorption curves through the equations of Laplace and Kelvin for the relationship between the partial vapour pressure and the pore water pressure. From measurements that indicate flow in the direction opposite to the gradient of vapour pressure the author concludes that the contribution of Fickian diffusion must be superimposed by that of capillary flow. Therefore the author suggests the use of a fictive water vapour permeability which combines the moisture resistance from dry cup measurements with the diffusion coefficient for high moisture levels. The author recommends the use of the profile method for obtaining the latter from transient measurements of moisture distribution (since it can, in contrast to the method of Boltzmann transformation, take into account the redistribution of moisture in the
material). For optimal resolution the moisture distribution can be measured with Nuclear Magnetic Resonance equipment. According to Krus this methodology is of special importance for capillary active materials that are exposed to driving rain.

Along the same line are the studies of Janz (2000). Janz gives an account of measurements of the relationship between suction and moisture content as well as the relation to the vapour pressure that is similar to the studies of Krus, but including a comparative study of various methods for measuring sorption isotherms. Janz does also discuss the different methods that are available for determining moisture transport coefficients at high moisture levels including a new cost effective method based on sorption measurements through stepwise solution of the diffusion equation for semi infinite media that are carried out for different initial condition for the moisture content.

Some authors have investigated the possibilities of deriving the relevant material properties of the material from its geometry. Examples are the work of Quenard et al. (1998) were the vapour diffusivity and permeability are derived from microstructure modelling based on scanning electron microscopy (SEM) images. Roels et al. (2002) did similar work using SEM to predict the moisture permeability with a multi-scale network model.

For the present purposes there is however no reason to incorporate the structural geometry of the material into the transport equations since the problem can be bypassed when the Dusty Gas Model is used and the subject is dismissed from this study.

The aim of the isotopic study was to show how the isotopic signature of water can be used to trace the origins of excessive water in buildings. The isotopes that have been used in this study are the naturally stable isotopes of oxygen-18 and deuterium as well as their better known sister isotopes of oxygen and hydrogen. There are several other isotopes to be found in water, some of which can help to unravel its history but those are not the subject of this study.
The method is illustrated with a case study of a building in the southern part of Sweden. A brief outline is given of the procedure of measuring the isotopic composition but the theoretical aspects of mass spectrometry are not the concern of this project.

It is also possible to use the differences in isotopic content to reveal which reactions are involved in the transport and fixation of water and water vapour in building materials. This is illustrated with experiments, where isotopic separation is measured for diffusion, capillary uptake and sorption. At this stage the focus is on developing an experimental method and verifying that method through experiments. The analysis of more complex reactions and the interaction of reactions will have to be the subject of future studies.

### 3. HISTORICAL BACKGROUND

#### 3.1 Diffusion

The random movement of microscopic particles suspended in gas or liquid is commonly referred to as Brownian motion or Brownian movement in honour of the Scottish botanist Robert Brown, which observed the phenomenon in 1828 while studying the fertilization process in *Clarkia pulchella* (see illustration on front page from Bailey, 1935), and recognized, in contrast to both predecessors and contemporaries, that the rapid oscillating movements of the pollen grains were not of organic character as could be verified through examinations of particles of glass and other inorganic material (Brush, 1976).

In the late 1870s it was widely believed that its cause was that of thermal molecular motion but until the contribution of Einstein in 1905 there was no quantitative theory that made it possible to test it against experiment (Brush, 1976).

Einstein took Stoke’s formula for the force acting on a spherical body moving in a viscous fluid from hydrodynamics and combined it with the formula for the osmotic pressure of dissolved molecules and arrived at his now famous result that the mean displacement of a Brownian particle is proportional to the square root of the time multiplied with the diffusion coefficient.
Einstein did this by using the methodology of statistical mechanics, going along the path that had been paved by Boltzmann, Maxwell and Gibbs and came to a result that shows how the macroscopic process of diffusion relates to the microscopic concept of thermal motion of individual molecules.

Smoluchowski came to a comparable result shortly thereafter, but by the means of a different method using kinetic theory and combinatorics and the results were verified by the experimental work of Perrin just a few years later (Brush, 1976).

The two equations that describe bulk diffusion were however known well before Einstein, from the work of the Swiss physiologist Adolf Fick, which had derived the fundamental laws governing diffusion by analogy with Fourier’s law of heat conduction (Fick, 1855), which were proven to be correct through the following laboratory experiments. The diffusion phenomena had however been observed previously by Graham in 1831 (Fick, 1855; Mason and Malinauskas, 1983), who carried out a uniform pressure diffusion experiment in which he demonstrated that the diffusive flow of gases is inversely proportional to the square root of their masses (because the flow is inversely proportional to the size of the pores and the collisions with the pore walls must be directly proportional to the mean molecular speed (and therefore the flux of two gases must be inversely proportional to their masses).

Graham was also the first to make an experimental observation of effusion, which is the flow of molecules due to a concentration gradient through pipes or pores with a diameter of a magnitude that is less than the mean free path of the molecules which means that the flow rate, which is governed by the size of the pores and the collisions with the pore walls must be directly proportional to the mean molecular speed (and therefore the flux of two gases must be inversely proportional to their masses).

A theoretical description of effusion was however put forward by Knudsen shortly thereafter which is why it is often referred to as Knudsen diffusion (Encyclopedia Brittanica Online, 2003)
The equation of Einstein has been used to describe concentration dependent diffusion coefficients, much notably so by Hill and then Higashi (Higashi et al., 1963) in their description of surface diffusion. The model was later modified by Okazaki et al. (1981) who included the time of residence at an occupied site into the equation for surface diffusion and showed how the activation energy of jumping can be retrieved from the sorption isotherms with the help of the Clausius-Clapeyron equation.

The so called Dusty gas Model of Evans, Watson and Mason can be used to describe the combined transport of gases due to effusion, viscous flow, continuum diffusion and surface diffusion. Mason and Malinauskas (1983) do however point out that the model is actually quite older, dating back to the work of Graham and later reinvented by Maxwell and then Deriagin and Bakanov.

3.2 Isotopes

Isotopes are species of atoms of a chemical element that share a position in the periodic table. The idea of isotopes was first put seriously forward by Soddy in 1910, which coined the term from the Greek isos, meaning “same” and topos signifying “place” (Aston, 1933). Isotopes have the same atomic number put differ in mass due to a different number of neutrons in the nuclei (the existence of the nuclei was not revealed until more than 20 years later (Clark and Fritz, 1997)). The idea originates from early studies of radioactivity, in which it had been observed that some elements with different masses were chemically indistinguishable and were therefore per definition of the same sort of element.

A few years later a definite proof of the existence of lighter and non-radioactive isotopes was given following the development of the mass spectrograph by Aston, which managed to confirm the previous observations of Sir Thomson that had indicated that neon was a mixture of isotopes with atomic weights of about 20 and 22 respectively (White and Wood, 1986)
Another very significant contributor to isotopic research was Urey whose early work on the subject includes the design of a method for concentrating any possible heavy hydrogen isotope by fractional distillation of liquid hydrogen which led to the discovery of deuterium in 1931 (Kirshenbaum, 1951). Urey did also carry out thorough studies of the thermodynamic properties of hydrogen and deuterium and the equilibrium constants of reactions involving their isotopes. From the thermodynamic development Urey went on to explain the differences in reaction rates for different molecular species and developed methods for using the effect of temperature on the fractionation factor for oxygen-18 to determine ocean temperatures as far as 180,000,000 years back.

Dansgaard investigated the abundance of $O^{18}$ in atmospheric water and water vapour (1953) and describes the correlation with temperature through a relationship between the vapour pressures of water molecules with $O^{16}$ versus $O^{18}$ and suggests a method for studying the mechanisms of precipitation by measurements of isotopic abundances. Dansgaard used a mass spectrometer, but it was only after World War II that spectrometers became more available, the previously most common method of measuring the isotopic abundance had been to use density tests. Dansgaard (1964) was also one of the pioneers in applying isotopic analysis in glaciological studies in which ice cores from the Greenland glacier have been used to investigate the changes in climate during the past 250 thousand years (Dansgaard et al., 1993).

Another active field of research is that of hydrology, where the abundance ratio of oxygen-18 and deuterium is used to describe and trace the hydrogeological cycle, which owes much to the work of Craig (1961), who published a landmark paper on the linear correlation between the abundance ratios of deuterium and oxygen-18 in meteoric waters.

Sveinbjörnsdóttir and Johnsen (1992) have done a study that illustrates the possibilities of using stable isotopes to determine the age and origins of groundwater and model the evaporation process.
4. METHODOLOGY

4.1 Moisture in constructions with loose-fill insulation and no vapour barrier

The houses are a part of an "environmental" building program that includes a neighbourhood of 44 apartments in the south of Stockholm. The measures that were taken in order to reduce the environmental impact include methods for reducing the consumption of water as well as choice of material. As a consequence of the latter the traditional polyethylene vapour barrier in the walls has been replaced with polypropylene fabric, which is a more diffusion open material.

In order to evaluate how this affects the moisture performance of the constructions, in-situ measurements of the moisture content and temperature in the walls, roofs and floors of three houses have been carried out. The measurements have been used to establish a model that can be used to predict the moisture performance for design moisture loads.

Measurements

The indoor temperature and relative humidity were registered continuously during 1997 and 1998 while the climatic conditions in the construction were measured about every three weeks in the same interval. The measuring points were place behind the outer gypsum board of the wall and underneath the wood panel of the “parallel” roof shown in figure 3 and are described in further detail in paper I.

The sensors were placed on the north walls and roof sides and on places where condensation was most likely to occur. The sensors were also placed in the floors on top of the concrete slab. Sensors on the outside of the constructions were placed in the piling foundation of 2 houses, in the crawlspace of one house, in the attic of two houses and at the eaves, as outdoor reference points.
A more detailed revision of the measurements is given in paper I.

Wall construction:
- 2x22 wood siding
- 28 ventilated air gap
- 9 gypsum board
- 250 cellulose fibre insulation between light-weight studs 600 oc
- 0.2 polypropylene fabric
- 22 spaced boarding
- 13 gypsum board

Floor construction:
- 25 wood flooring
- 32 spaced boarding
- 70+180 cellulose insulation between studs 600 oc
- 60 concrete

Roof construction:
- Concrete tiles on battens
- 1 roofing felt
- 19 wood panel
- 195 cellulose fibre insulation between joists 1200 oc
- 0.2 polypropylene fabric
- 22 spaced boarding
- 13 gypsum board

Figure 3 Roof, wall and floor constructions in the houses (measures in mm).

Hourly values of outdoor temperature, relative humidity, wind speed and direction and solar radiation were taken from a nearby climatic station operated by the city of Stockholm.

Calculation model
The model used for simulating the moisture condition in the constructions is a numerical solution of Fick’s first law for diffusion under transient conditions, where the sorption properties of the materials are taken into consideration and the moisture transport is assumed to be purely diffusive. Solar radiation is not taken into account. When calculating the temperature distribution the conditions are assumed to be steady-state and daily averages are used. All flows are assumed to be one-dimensional.

In principle, calculations have been carried out with the forward difference method as described in paper I. The vapour permeability of the materials is assumed to be constant.

In short, the vapour concentration is calculated in every time step (day) from the relative humidity, which, by using the inverse of the function describing the sorption isotherm, can be based on the water content of the previous day.
The net flow, \( \Delta g_j \) [\( \text{kg/m}^2\cdot\text{s} \)], into node j can then be written

\[
\Delta g_j = \left( \frac{\nu_j - \nu_{j-1}}{Z_j} \right) + \left( \frac{\nu_j - \nu_{j+1}}{Z_{j+1}} \right) \tag{1}
\]

where \( \nu_{j-1} \), \( \nu_j \) and \( \nu_{j+1} \) are the vapour concentrations [\( \text{kg/m}^3 \)] of the previous node, the node in question and the next node, in that order, whereas \( Z_j \) and \( Z_{j+1} \) are the moisture resistances [\( \text{s/m} \)] of the thread preceding the node and the one behind it. This gives an accumulated water content \( \Delta w \) [\( \text{kg/m}^3 \)], over the period \( \Delta t \) [\( \text{s} \)] that for a node of width \( \Delta x \) [\( \text{m} \)] can be written:

\[
\Delta w_j = \Delta t \cdot \frac{1}{\Delta x_j} \cdot \left( \frac{\nu_j - \nu_{j-1}}{Z_j} + \frac{\nu_j - \nu_{j+1}}{Z_{j+1}} \right) \tag{2}
\]

The results of the simulations are shown in the next chapter.

### 4.2 Tracer gas measurements

The ordinary diffusion coefficient and the Knudsen diffusion coefficient can be described with explicit functions of the textural properties of the porous material and the thermodynamic properties of the gases. Consequently the diffusion coefficients for water vapour can be calculated from the measured diffusion coefficients for tracer gas, provided that it is possible to differentiate between the contributions of the two diffusive flow mechanisms. This can be done with the dusty gas model of Mason and Malinauskas (1983) that makes it possible to use a series of tracer gas measurements to obtain the so called DGM material parameters of a porous material that control the flow in vapour phase due to ordinary diffusion, Knudsen diffusion and viscous flow.

It is well known that some materials exhibit a strong concentration dependency of the diffusion coefficient (Nevander and Elmarsson, 1994). As shown in the measurement results of Abbas (2000) the diffusion coefficient is also exponentially dependant on temperature.
This is something that characterises an activated process and it is therefore natural to approach the problem by the Random Hopping Model of surface diffusion that describes the diffusion coefficient as a function of the amount adsorbed as well as the energies required to activate jumps between sorption sites.

![Figure 4 The transport processes](image)

Since the process of surface diffusion involves interactions of the water with the pore walls of the material it is best measured with complementary measurements as described at the end of this section.

**Ordinary diffusion**
The ordinary diffusion of a gas through a porous material is driven by the concentration gradient and must depend on the diffusion coefficient of the gas for that material, i.e. the flow rate per unit area of a section can be written as

$$F = -D_{\text{gas}} \frac{dC}{dx}$$  \hspace{1cm} (3)

where $D_{\text{gas}}$ is the diffusion coefficient of the gas in the material, $C$ is the concentration and $x$ is the coordinate normal to the section. The diffusion coefficient depends on the diffusion coefficient of the gas in free air, $D_{\text{gas}}^{\text{air}}$, as well as the porosity of the material $\varepsilon[-]$ and its tortuosity, $\tau^\prime[-]$, which is a measure of how much a pore deviates from a straight line through the material (Mason and Malinauskas, 1983), or
\[ D_{gs} = \left( \frac{\varepsilon}{\tau} \right) D_{\text{gas}}^{\text{air}} \]  

(4)

Hence, the ordinary diffusion coefficient of the porous material for water vapour can be calculated from the measured tracer gas diffusion coefficient under the assumption that textural properties of the material, that is, the porosity and the tortuosity are the same for both gases, or

\[ D_{\text{water vapour}} = D_{\text{water vapour}}^{\text{air}} \cdot D_{\text{tracergas}} \]  

(5)

The ratio of the diffusion coefficient of water vapour to that of tracer gas is most easily calculated by using empirical values that can be obtained from the literature. Massman (1998) has studied measurement results of the molecular diffusivities of several gases near STP, including both dinitrogen oxide and water vapour in air. The result is a recommended value of \(21.78 \cdot 10^{-6} \text{ m}^2/\text{s}\) for water vapour in air and \(14.36 \cdot 10^{-6} \text{ m}^2/\text{s}\) for dinitrogen oxide which gives a ratio of about 1.517 although it must be kept in mind that the information is based on a limited number of experiments.

**Knudsen diffusion**

When a relatively large number of the pores have dimensions that are similar or smaller than the mean free path of the water vapour molecule in air the diffusion process is governed by the collisions of the molecules with the pore walls, and is known as Knudsen diffusion or effusion.

For different gases with the same mode of scattering an effective Knudsen diffusion coefficient, \(D_{ik} \text{ [m}^2/\text{s}]\), can be written (Mason and Malinauskas, 1983):

\[ D_{ik} = \frac{4}{3} K_0 \left( \frac{8 \mathfrak{N} T}{\pi m_i} \right)^{1/2} \]  

(6)

regardless of the nature of the collisions, where \(\mathfrak{N}\) is the ideal gas constant [J/mol·K], \(T\) is the temperature [K] and \(K_0\) is constant for all gases that have the same mode of
scattering, regardless of the nature of the collisions, but varies with the material. This makes the ratio of the Knudsen diffusion coefficients equal to the square root of the inverse ratio of their masses and the Knudsen diffusion coefficient for water vapour can be written

$$D_{\text{water},K} = \sqrt{\frac{m_{\text{tracer gas}}}{m_{\text{water}}}} \cdot D_{\text{tracer},K} \quad (7)$$

If the mean free path of a water molecule, which has an order of magnitude of about $10^{-8}$ m (Krus, 1995; Andersson, 1984), is compared to the pore size distribution of some well known porous building materials (keeping in mind that pore size is difficult to define) it is reasonable to assume that the contribution of Knudsen diffusion should be of significance when the diffusive flow through concrete, wood and limestone is considered. The values given for the pore size distribution of the other materials, such as light concrete, light aggregate concrete and brick suggest, however, that the contribution of ordinary diffusion is of much greater importance. Ultimately it must be up to experiment to determine the relative magnitude of each process.

**Combined transport and the DGM material parameters**

In order to get the complete DGM transport equations Mason and Malinauskas start by connecting the assumingly independent diffusive flows in series and then add the viscous flow contribution, as shown in figure 5 below. They assume that even the flow due to surface diffusion is independent and connected in parallel with the other flow mechanisms.

The resulting transport equations can under isothermal conditions be written (Mason and Malinauskas, 1983; Tuchlenski 1983):

$$\sum_{j=i}^{v} x_i N_j \cdot \frac{N_i}{PD_{ij}} \cdot \frac{1}{\eta \text{D}_{i,K}} \cdot \nabla x_i + \frac{x_i}{P \eta \text{D}_{i,K}} \left( \frac{B_{ii}P}{\eta \text{D}_{i,K}} + 1 \right) \nabla P \quad (8)$$
where the original notations have been used and $N$ is the molar flux [$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$], $D_{ij}$ is the binary diffusion coefficient of gas $i$ in gas $j$, $P$ is the absolute pressure [Pa], $\eta$ is the dynamic viscosity [Pa·s], $B_0$ is the permeability constant [m$^2$] and $x_i$ [-] is the mole fraction.

Figure 5  Combined transport

By adding the pair of equations we get from (8) we get the following (Mason and Malinauskas, 1983; Tuchlenski 1983):

$$N - \left(1 - \frac{D_{1K}}{D_{2K}}\right) \cdot N_2 = \frac{D_{1K}}{\gamma RT} \left(1 + \frac{B_0 P}{\eta}\right) \sum_{i=1}^{2} \frac{x_i}{D_{iK}} \nabla P$$  \hspace{1cm} (9)

Measurements of the left hand side of equation (9) over the pressure difference plotted as a function of the total pressure will therefore be straight lines whose gradient gives the permeability whereas the interception with the axes gives the Knudsen diffusion coefficient. The binary diffusion coefficient can then be calculated from equation (8). These measurements of the DGM transport coefficients can be carried out with a non adsorbing gas, while complementary measurements will be needed to evaluate the contribution of surface diffusion.
Measurements of the water vapour permeability with N$_2$O

Dinitrogen oxide was chosen for the experiments since it is non hazardous and easily detectible. An attempt was made to separate the contribution of ordinary diffusion and Knudsen diffusion but with the equipment at hand it proved out to be impossible as described in Abbas (2000).

For a serially coupled diffusion processes the effective diffusion coefficient of water can be written as

$$\frac{1}{D_{\text{water,eff}}} = \frac{1}{D_{\text{k}}} + \frac{1}{D_{\text{water,air}}}$$

(10)

Furthermore the ratio of the Knudsen diffusion coefficients is numerically about the same as the ratio of the ordinary diffusion coefficients for N$_2$O and water which makes it is possible to obtain the effective diffusion coefficient, $D_{\text{eff}}$ in a single measurement from the following equation

$$\frac{1}{D_{\text{water,eff}}} = C_{\text{eff}} \left( \frac{1}{D_{\text{k}}} + \frac{1}{D_{\text{water,air}}} \right)$$

(11)

where $C_{\text{eff}}$ is the ratio of the ordinary diffusion coefficient in air and is in the case of N$_2$O and water approximately equal to the ratio of the Knudsen diffusion coefficients.

The measurement that are described in more detail in paper IV were carried out by placing a specimen of the material to be tested on top of a container with tracer gas and monitoring how the concentration declines with time when zero concentration is maintained at the upstream side.

According to Björk et al. (1997) the transport resistance of a material with no vapour storage, $Z_c$ [s/m] can then be calculated from the following equation

$$Z_c = \frac{A}{V} \cdot \frac{t}{\ln \frac{c_0}{c_i}}$$

(12)
where $c_0 \,[\text{ppm}]$ is the concentration at the upstream side of the porous material at the start of the test, $c_t \,[\text{ppm}]$ is the concentration at the time $t \,[\text{s}]$, $A$ is the area open to diffusion $[\text{m}^2]$ and $V$ is the volume $[\text{m}^3]$ of the test chamber. The tracer gas permeability $D_{\text{tracer gas}}$ can then be obtained by dividing the thickness of the material by the transport resistance. From equation (5) the water vapour permeability can then be calculated. The results are shown in the next chapter.

**Surface diffusion**

According to the random hopping model of Higashi (1963) surface flow can be modelled as a diffusion process, in which the molecules jump between sorption sites. Consequently, since diffusion is a random walk process, the surface diffusion coefficient must be directly proportional to the square of the distance between sorption sites and inversely proportional to the time between jumps (Hecht, 1990). The time between jumps can be approximated by the time of residence for a hopping molecule that must depend on the number of molecules with sufficient activation energy for jumping in relation to the total number of molecules that have less energy than required to be desorbed. Hence, the mean time of residence can be obtained by integrating over the energy distribution function which according to Okazaki et al., that has modified the original equation of Higashi by including not only the residence time in the first layer but also that of the layers above, gives the following equation for the surface diffusion coefficient (Okazaki et al. 1981)

$$D_s = D_{s0} \left( \frac{\theta}{\Theta} \right) \left( e^{-\frac{E_{s1}}{RT}} - e^{-\frac{E_{ao}}{RT}} \right) \left( 1 - e^{-\frac{E_{ao}}{RT}} \right) \left( 1 - \frac{\tau_1}{\tau_0} \right) \left( 1 - e^{-\frac{E_{s1}}{RT}} \right) \left( 1 - e^{-\frac{E_{ao}}{RT}} \right)$$

(13)

where

$$\frac{\tau_1}{\tau_0} = \left( e^{-\frac{E_{ao}}{RT}} - e^{-\frac{E_{s1}}{RT}} \right) \left( 1 - e^{-\frac{E_{ao}}{RT}} \right) \left( e^{-\frac{E_{ao}}{RT}} - e^{-\frac{E_{s1}}{RT}} \right) \left( 1 - e^{-\frac{E_{s1}}{RT}} \right)$$

(14)

and $\theta$ is the effective surface coverage, $E_{ao}$ $[\text{J/mol}]$ is the differential heat of adsorption, $E_{s1}$ $[\text{J/mol}]$ is the heat of adsorption for the second layer and all layers above it that is assumed to be equal to the heat of liquefaction and $E_{s1}$ $[\text{J/mol}]$ is the activation energy of
migration. The constant \( a \), is the ratio between the heat of adsorption and the activation energy in the first layer.

In equation (13) it is assumed that the differential heat of adsorption \( E_{a0} \) is independent of the amount adsorbed, which holds for an energetically homogenous surface. For an energetically heterogeneous surface the differential heat of adsorption will on the other hand vary with the amount adsorbed which means that equation (13) has to be integrated over the range of the heat of adsorption.

The flow rate of surface diffusion, \( F_s(t) \text{ [g/m}^2\text{s]} \) can then be written as

\[
F_s(t) = -D_s \cdot \frac{\partial S}{\partial x} \tag{15}
\]

using the diffusion coefficient of equation (13) and the driving potential is the amount adsorbed, \( S \text{ [g/m}^3\text{]} \), but given the relationship to the other state variables of moisture, the concentration \( v \text{ [g/m}^3\text{]} \) or the moisture content, \( w \text{ [g/m}^3\text{]} \) might as well have been chosen. In order to calculate the potential surface flow we therefore have to estimate the energies involved in absorption and activation of the water molecules and the different amounts absorbed for varying partial pressures. In other words, estimate the values of \( \theta_e \), \( E_{s1} \), \( E_{a1} \) and \( E_{a0} \) of equations (13) and (14).

When an adsorption isotherm obeys the BET equation, the effective surface coverage can be expressed by equation (16)

\[
\theta_e = \theta(1-\varphi) \tag{16}
\]

where \( \varphi \) is the relative pressure \([p/p_s]\) and \( \theta \) is given by:

\[
\theta = C_{\text{BET}} \varphi /((1 - \varphi)(1 - \varphi + C_{\text{BET}} \varphi)) \tag{17}
\]
where $C_{\text{BET}}$ is a constant. It is assumed that the surface migration has a small influence on the adsorption equilibrium, in which case they can be applied to estimate $\theta_e$. The heat of vaporisation $E_{a1}$ can be found in the literature (CRC handbook, 2001). The activation energy for migration $E_{s1}$ may be approximately estimated with the Frenkel equation (Okazaki et al. 1981) that relates the temperature dependency to viscosity in the liquid state, $\mu_L \text{[Pa} \cdot \text{s]}$ and can be found in the literature (CRC handbook, 2001).

The isosteric heat of adsorption $E_{st}$ is determined from adsorption isotherms at various temperatures using the Clausius Clapeyron equation (Okazaki et al., 1981):

$$E_{st} = -\mathcal{R} \cdot \left( \frac{\partial \ln p_v}{\partial (1/T)} \right)_w$$

(18)

where $p_v$ is the partial pressure of water vapour that corresponds to a certain moisture content, $w \text{[kg/m}^3\text{]}$ and $T$ is the temperature for that moisture content and partial pressure or the corresponding relative humidity.

![Figure 6](image-url)  

**Figure 6**  The parameters needed to determine the isosteric heat of adsorption with help of the Clausius-Clapeyron equation.
The isosteric heat of adsorption contains both the effects of $E_{a0}$ in the first layer and $E_{a1}$ in all the layers above, in the case of multilayer adsorption.

If the adsorption equilibrium obeys the BET equation (Okazaki et al., 1981),

$$E_{a0} = \frac{(E_{st} - \theta T - \varphi E_{a1})}{(1-\varphi)} \quad (19)$$

while when multilayer adsorption does not take place,

$$E_{a0} = E_{st} - \theta T \quad (20)$$

Equation (13) can therefore be used to describe the surface flow coefficient as a function of the amount adsorbed and temperature in the range from less than monolayer to multilayer adsorption.

For a full description of the diffusion coefficient of equation (13) it is however necessary that the constant coefficients $D_{s0}$ and $a$ are obtained. This can be done with either a series of steady state measurements or through transient measurements using the time-lag method as described in paper II. The time lag method makes it possible to obtain the constant coefficients as long as the functional form of the diffusion coefficient is known even though there is no general analytical solution to the diffusion equation when the diffusion coefficient is a function of concentration. In both cases it is assumed that the total flow is the sum of the flow due to diffusion and surface diffusion and that these processes are approximately independent.
4.3 Isotopic analysis

Definitions

A term generally used to denote the isotopic content, is the abundance ratio, R, or the ratio of the heavier to the light isotope, for example the ratio of oxygen-18 to its more frequently encountered sister isotope of oxygen-16. The most common way of referring to the measured isotopic content of a sample is however the δ-value, which is the difference between the abundance ratios of the sample and the reference over the measured ratio of the reference. This can be written as:

$$\delta = \left( \frac{R_{\text{sample}}}{R_{\text{reference}}} - 1 \right) \cdot 1000 \%$$ \hspace{1cm} (21)

In the case of oxygen-18 the δ-value becomes:

$$\delta = \left( \frac{^{18}O/^{16}O}_{\text{sample}} - \frac{^{18}O/^{16}O}_{\text{reference}} \right) \cdot 1000 \%$$ \hspace{1cm} (22)

The greater the δ-value the more it contains of the heavier isotope and a positive δ$^{18}$O‰ value, say +10‰, means that the sample is heavier than the reference by 1 percent. The reference customarily used for the abundance ratios of oxygen-18 to oxygen-16 as well as deuterium to hydrogen is the VSMOW or Vienna Standard Mean Ocean Water (Clark and Fritz, 1997). The reference that originates from the International Atomic Energy Agency is hypothetical. For practical reasons, it is sometimes more feasible to use local water as a reference after it has been calibrated with a sample of VSMOW.

But, even though the environmental isotopes of hydrogen and oxygen are stable, physical and chemical reactions can cause changes in the isotopic content because of the different reaction rates of water molecules with different isotopic composition.
This change is expressed by the fractionation factor $\alpha$, which is the ratio of the abundance ratios for the reactant and the product:

$$\alpha = \frac{R_{\text{reactant}}}{R_{\text{product}}}$$

(23)

As an example, the evaporation of water the fractionation factor for oxygen is:

$$\alpha^{18O}_{\text{water-vapour}} = \frac{\left(\frac{^{18}O}{^{16}O}\right)_{\text{water}}}{\left(\frac{^{18}O}{^{16}O}\right)_{\text{vapour}}}$$

(24)

and since the evaporation process favours the lighter molecules the fractionation factor will be greater than 1 while a reaction that has a preference for the heavier isotope will yield a fractionation factor less than 1.

The isotopic difference in parts per thousand is defined as

$$\varepsilon_{\text{reactant/product}} = \left(\frac{R_{\text{reactant}}}{R_{\text{product}}} - 1\right) \cdot 10^3 = (\alpha - 1) \cdot 10^3$$

(25)

and subsequently a reaction that favour the lighter isotope has a positive isotopic difference. The isotopic separation, $\Delta$, between two compounds, $X$ and $Y$, is defined by the following equation

$$\Delta_{X-Y} = \delta_X - \delta_Y$$

(26)

The $\Delta$ values can be calculated for any two compounds, whether they are reacting or not, and are used for a comparison of the measured separation with the calculated isotopic difference.
Meteoric line

Of great importance is the well known global correlation between the δ-values of deuterium and oxygen-18 for fresh surface waters that was discovered by Craig (1961) and shown in figure 7.

![Global Correlation between δD and δ18O](image)

$$\delta D = 8\delta^{18}O + 10$$

**Figure 7** The global correlation between the δ-values of deuterium and oxygen-18 according to Craig (1961).

This relationship can be explained by the different vapour pressures of H$_2^{18}$O and HDO that give a ratio of about 1 to 8 between the δ-values of deuterium and oxygen for condensation at equilibrium. Craig’s global meteoric water line is the average of many local meteoric water lines and local deviations, due to climatic factors as for example the origin of the vapour mass and seasonality, are to be expected.
Since we also know from the work of Dansgård that the temperature is known to correlate with \( \delta^{18}O \) of the precipitation (Clark and Fritz, 1997) the position on the meteoric line can be determined from the temperature at rainout.

**Rayleigh processes**

When the product of a reaction is continuously removed it will lead to exponential enrichment or depletion of the residual reservoir (McCabe and Smith, 1976; Clark and Fritz, 1997). This is commonly referred to as a Rayleigh-type evolution. For a Rayleigh type process the isotope ratio, \( R \), of a diminishing reservoir is a function of the isotope ratio of the reservoir at the start of the reaction, \( R_0 \), the fraction left of the reservoir, \( f [-] \), as well as the fractionation factor for the reaction, \( \alpha \)

\[
R = R_0 \cdot f^{(\alpha-1)}
\]

(27)

This means, as an example, that as the product of a reaction that favours the lighter isotope is continuously removed the reservoir of the reactant will get heavier as it decreases in size. A number of isotopic reactions follow a Rayleigh-type evolution, for example the change in the abundance ratios of oxygen-18 and deuterium during evaporation of water at non-equilibrium conditions.

**Experimental procedure**

Isotopic analysis will inevitably start with sampling of the water. It is best that the samples are kept in air tight glass bottles and frozen in order to avoid reactions that may alter their isotopic composition. In the case study of this project the samples were sent to the laboratory of the Division of Geophysics at the Science Institute of the University of Iceland. The laboratory procedure can be briefly outlined as follows. The \( ^{18}O \) content of the water is measured by equilibrating the water with CO\(_2\) and then analysing the CO\(_2\), by mass spectrometry. The fractionation factor of this reaction is known since previously. The accuracy of determining the \( ^{18}O \) content in this manner is better than \( \pm 0,03\% \). The deuterium content of the samples is measured by a method resembling that of Coleman et al. (Coleman et al., 1982). 2 \( \mu l \) of degassed water are reduced to hydrogen
with 15 mg of zinc metal in a sealed quartz tube at about 450°C for 10 minutes. The zinc pellets are then heated up to 700°C in order to transfer the remains of the zinc to the walls of the sample tubes by evaporation and condensation. Then the samples are again kept at 450°C for 20 minutes. The hydrogen gas is then analysed by mass spectrometry. The precision of the measurements is 0.7‰. The reference used is local water that has been calibrated with a sample of VSMOW.

**Isotopic analysis of excessive water**

In order to determine the origins of excessive water a sample of the water is taken and its δ-values measured. When possible, it is of advantage to collect samples of water from the possible sources for comparison.

On the occasions when the δ-values of the sample match that of a possible candidate the origins of the excessive water will be revealed directly. When not, further studies have to be conducted.

Of central importance is the relation between the δ-values of oxygen-18 to those of deuterium in relation to the local meteoric water line.

In those instances when the measured δ-values coincide with the meteoric line it can be assumed that the water in question is fresh surface water. Hence the number of possible candidates has at least been reduced to those that originate from rainwater and have not undergone reaction (apart from evaporation and condensation at equilibrium). This means that even without a sample from the possible sources isotopic analysis can give some information about the sources of excessive water. If known, the temperature at rainout for the different possible sources can also be used to determine the position a sample of freshwater should have on the meteoric line.

A deviation from the meteoric line will on the other hand indicate that the water has undergone a reaction.
In that case the next step will be to calculate the isotopic differences for the most plausible reactions and then to compare those to the measured isotopic separation between the excessive water and the possible candidates.

The results of a case study in which isotopic analysis has been used to identify a possible source of excessive water are presented in the next chapter of this thesis. A more thorough description of the study is to be found in paper III.

In the next section of this paper the effects of some common reactions on the isotopic content is described. It is also explained how isotopic analysis can be used to evaluate the contribution of the different physical processes as water or water vapour is transferred through building materials.

**Isotopic analysis of reactions**

Some reactions will cause isotopic enrichment of the heavier isotopes while other lead to depletion but the magnitude will vary as well as the ratio of the isotopic difference of deuterium over that of oxygen-18. This is because not only are the thermodynamic properties of ordinary water different to those of water containing the heavier sister isotopes, but there is also a difference in the physical properties of water consisting of H$_2^{18}$O and those that consist of HDO molecules.

When the water undergoes condensation or evaporation the ratio between the isotopic differences of oxygen-18 and deuterium is for instance determined by the relationship between their vapour pressures (the slope must equal that of the meteoric line). In the case of diffusion and effusion the ratio will on the other hand be determined by the mass ratios, which makes the magnitude of isotopic difference greater for effusion as explained in paper V. Non separative processes such as convective flow, and assumingly capillary flow, will however result in no isotopic difference.

Consequently the measured isotopic separation over a specimen can be used to describe the relevance of different transport processes and ultimately to it will be possible to use
isotopic analysis to revise or refine the existing models of moisture transport in building materials.

![Diagram](image)

**Figure 8** The isotopic differences of deuterium vs. oxygen-18 for some common reactions

As an example the contribution of effusion versus that of ordinary diffusion can be investigated by carrying out an experiment in the lower hygroscopic region (in the absence of capillary transport). The magnitude of the isotopic separation between sample points B and F in figure 9 would then be determined by the relative contribution of ordinary diffusion versus that of effusion. The same experiment could then be conducted in the upper hygroscopic region in order to evaluate the relevance of capillary transport, the contribution of which could be noted by an increase in the overall flow but without an increase in isotopic separation.

Further insight can be gained by comparing the isotopic content of points C, D and E in figure 9. The isotopic content of those should for instance be the same for a capillary transport process running in parallel to the diffusive processes. If these processes were
however to be modelled as connected in series, i.e. diffusion below the critical moisture content and capillary transport through the remaining part, the isotopic content should change in the direction of flow as far as the material is beneath the critical moisture content while the abundance ratios remain constant throughout the capillary region.

![Diagram](image)

**Figure 9** A schematic view of sample points for isotopic analysis of moisture transport through a material

The experimental results that are illustrated in this thesis include a comparison of the measured isotopic separation and the calculated isotopic differences for ordinary diffusion as well as adsorption and capillary uptake and are the first steps in developing a method for analysing transport processes through measurements of isotopic composition.

One of the challenges is to construct an experiment, the effects of which on the isotopic content are none or that can be calculated and taken into account.

**Adsorption and capillarity**

In the first attempt to measure the isotopic separation through adsorption and capillary uptake the moisture was extracted from the specimens with a distillation process. In short the specimen, that measured 8 by 8 by 4 cm$^3$ and consisted of light aggregate concrete, were conditioned in a closed container, by either capillary uptake or adsorption, and then placed in a reaction vessel within a climatic chamber at 105°C from which the
evaporating water was led to a condenser and collected in a test tube as described in (Gudmundsson, 2002). This study was inconclusive but the ratio of the isotopic separation suggests fractionation caused by the difference in vapour pressure, most likely due to the experimental method. In the next step of the study the problem was bypassed by evaluating the effects of reactions by measuring the isotopic content of the remaining water.

The capillary experiment was carried out by placing the specimens in direct contact with the water and within a vessel as shown in figure 10. After 24 hours a sample was taken of the remaining water that had been reduced to about half of its amount. The results of the measurements are given in chapter 5.

Figure 10  The experimental setup for the capillary uptake and sorption experiment

The amount adsorbed in the material was consistent with the sorption experiments carried out by Abbas (2000) and by weighing the vessel it was confirmed that the mass of the system was conserved through the experiment.

Diffusion experiment

A series of wet-cup measurements were carried out in order to evaluate the isotopic separation for a pure ordinary diffusion process. The specimens consisted of a sheet of
mineral wool, with a thickness of 12 cm and were placed on top of cups made of HDPE plastic and with a square area of 17×27 cm². In order to reduce the edge effects the specimens were placed within plastic cups of the same material from which the bottom had been removed. The cups were partly filled with water and placed in a climatic chamber with a temperature of 20 ° C and at a relative humidity of 50%. Samples of the remaining water were then collected for analysis of the isotopic content.

Figure 11  The calculated ratio of abundance ratios, \( R/R_0 \), for evaporation following a Rayleigh type evaluation as a function of the fraction left of the reservoir, \( f \).

It was assumed that the reactions follow a Rayleigh-type evolution where the fractionation factor is the multiplicity of the fractionation factors for evaporation in the cups and for diffusion through the material as shown in figure 11.

This means that the abundance ratio of the remaining water increases exponentially as the reservoir gets smaller and can be calculated with equation (27).
5. RESULTS

5.1 Measurement results for construction with no vapour barrier

The measurement results for the relative humidity are shown in Figures 12 to 14, where the relative humidity is plotted against the number of days from February 2\textsuperscript{nd} 1997. As a reference, the relative humidity at the eaves of house 21 is also shown in figure 12.

![Figure 12](image12.png)

Figure 12 Measurement values of relative humidity in wall, floor and at the eaves of house 21.

![Figure 13](image13.png)

Figure 13 Measurement values of relative humidity in wall, roof and floor of house 85
As shown in the previous figures there seems to be no cause for alarm in any of the constructions. It must be noted however that these measurement results correspond to the actual climatic conditions (not so severe moisture production) and it was of great interest to investigate by simulations how the constructions would behave when a design moisture load and a standard reference climate are used. But first the model had to be verified using actual data as shown in the next section.

5.2 Calculation model for construction with no vapour barrier

The climatic data used for verifying the model is the actual daily mean values of vapour concentration and temperature.

A description of the material properties including the thermal conductivity, moisture permeability and approximations to sorption curves is to be found in paper I.

The validity of the model was verified by comparing the calculation results with the measurements for a period of two years starting on February the second 1997. The results for the wall of house 21, the roof of house 85 and the floor of house 85 are shown below.
Figure 15  Measured vapour concentration vs. calculated for the wall of house 21.

The same type of calculation has been carried out for the roof of house 85. The results are shown in Figure 16.

Figure 16  Measured vapour concentration vs. calculated for the roof of house 85.
The simulated conditions for the roof did not show as good an agreement with the measurements. There was no clear indication of natural or forced convection in the roof construction. The conditions for the floor in House 85, where piling foundation was used, show a relatively good correlation between the model and the measurements as shown in Figure 17.

![Figure 17](image)

**Figure 17**  Measured vapour concentration vs. calculated for the floor of house 85.

### 5.3 Simulation for construction with no vapour barrier

As the model gave fairly good agreement with the measurements of the floor of House 85 and the walls of all houses, a 5-year simulation was carried out to see how the constructions would perform under design moisture load and for reference weather conditions. The climatic conditions used in the simulation are based on monthly mean values for the weather station in Bromma and values taken from (Nevander and Elmarsson, 1994). The results of the 5-year simulation for the wall construction are shown in figures 18 and 19 and for the floor constructions in figures 20 and 21. Two different moisture loads were used, 2 and 4 g/m$^3$. The moisture loads were assumed to be constant throughout the year. The node in the gypsum board lies in its middle, whereas the node in the cellulose fibre is 31 mm from the inside of the outer gypsum board.
Figure 18  5-year simulation of wall, for a moisture supply of 2 g/m$^3$.

Figure 19  5-year simulation of wall, for a moisture supply of 4 g/m$^3$.

The significance of the calculated moisture conditions shown in Figures 18 and 19 was evaluated by counting the number of days when a certain temperature is exceeded at the same time as the humidity rises above a certain level, thus making mould growth feasible.
Figure 20 5-year simulation of floor, for a moisture supply of 2 g/m$^3$.

Figure 21 5-year simulation of floor, for a moisture supply of 4 g/m$^3$.

Using the curve of (Nevander and Elmarsson, 1994) these criteria were set to a temperature of 8°C and a relative humidity of 70% for a moderate risk of mould growth and 85% for a high risk of mould growth. The results for the wall construction are shown in figure 22.
Figure 22  Mould growth risk analysis for the wall construction. Number of days when the criteria of high and moderate risk is met for the moisture loads of 2 g/m$^3$ and 4 g/m$^3$.

5.4 Tracer gas measurements
The results of the tracer gas measurements are shown in the following table in which the calculated water vapour permeability is compared with the results from the wet- and dry-cup measurements. The ratio of the molecular diffusivities of dinitrogen oxide and water vapour is 1,517, which is based on the values recommended by Massman (1998).

<table>
<thead>
<tr>
<th>material</th>
<th>$\delta_{\text{tracer}}$</th>
<th>$\delta_{\text{v,calc}}$</th>
<th>$\delta_{\text{v}}$</th>
<th>$\delta_{\text{v}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_1 = 866$ kg/m$^3$</td>
<td>0,91</td>
<td>1,38</td>
<td>1,47</td>
<td>1,23</td>
</tr>
<tr>
<td>$\rho_2 = 552$ kg/m$^3$</td>
<td>3,61</td>
<td>5,47</td>
<td>5,71</td>
<td>3,46</td>
</tr>
</tbody>
</table>

$^{1}$From Abbas (2000)

The results indicate that the water vapour permeability can with a good degree of accuracy be calculated from the measured tracer gas permeability. It is worth mentioning that calculations according to the empirical approximation of Chen and Othmer to the
Chapman-Enskog theory of the molecular diffusivities would have given a ratio of about 1.40 and that a similar value would have been obtained from the Chapman-Enskog/Lennart-Jones model (Massman, 1998). For the material with the higher density this would have resulted in a difference of about 3.5% between the value obtained from tracer gas measurements and the dry cup measurements.

The author repeated the tracer gas measurements for both materials and the resulting calculated water vapour permeability was $1.94 \cdot 10^{-6}$ m$^2$/s and $4.32 \cdot 10^{-6}$ m$^2$/s for the heavier and the lighter material respectively. It must be born in mind that both methods involve an error of measurement.

A review of experimental error when the cup-method is used can be found in Bomberg et al. (2002). In order to investigate the possible effect of tracer gas solubility on the results some measurements were carried out using dried out material as described in paper IV. The results indicate that the solubility of the gas has no significant effect on the results.

The results of Abbas (2000) work also show that the diffusion coefficient is exponentially dependent on temperature. As indicated by the difference in dry- and wet-cup measurements, the latter showing a much stronger dependency, this behaviour cannot be explained with the temperature dependency of the ordinary diffusion coefficient and therefore it is justified to assume that the diffusion mechanism in question is an activated process, which supports the choice of using the Random hopping model of surface diffusion. In the next section the measurements that were carried out in order to evaluate the activation energies of surface diffusion are revised.
5.5 Sorption measurements

The sorption experiments were carried out for the heavier material, with density of 866 kg/m$^3$, as described in Abbas (2000) and in figure 23 it is shown how the adsorbed amount of moisture changes with relative humidity for the temperatures of 21°C and 60°C.

From the sorption isotherms shown in figure 23 it is possible to calculate the activation energies of migration, $E_{a0}$, as described by equations (18) and (19) under the assumption that the BET-equation is valid.

![Sorption Isotherms](image)

**Figure 23** Sorption isotherms for 21°C and 60°C.

The next step was therefore to carry out a log linear regression to the BET-equation that resulted in the curve shown in figure 24 together with the actual measurement values for 21°C on the basis of which it was determined that the assumptions of the BET-theory required to calculate the activation energy from the previous figure were legitimate.
5.6 Activation energy and surface diffusion

After obtaining the heat of adsorption from the sorption isotherms with help of the Clausius-Clapeyron equation the activation energy of migration, $E_{a0}$ can be calculated. Equation (13) can then be used to calculate the surface diffusion coefficient as a function of the constant coefficient $D_{s0}$. This was done by approximating the activation energy as a stepwise function in 4 intervals corresponding to moisture content in the range of 10 to 35 kg/m$^3$. The diffusion coefficient for each relative humidity is then obtaining by weighing the terms of equation (13) in each interval with the amount adsorbed. It is estimated that the constant $a$ has a value of 0.5. The results are shown in the figure below.

Figure 24  Measured moisture content, $w$ [kg/m$^3$] vs. relative humidity according to BET-theory

![Graph showing measured moisture content vs. relative humidity according to BET-theory]
The resulting curve shows the familiar exponential dependency of the coefficient of surface diffusion. This exponential dependency has also been confirmed through isothermal steady state cup measurements that have been carried out at different temperatures (Abbas, 2000), the results of which are shown in paper IV.

What remains to be done is to obtain the constant coefficient $D_{s0}$. This could be done by complementing a tracer gas measurement with a wet cup measurement in a narrow interval at a high relative humidity. The tracer gas measurement is assumed to give an estimate of the pure Fickian contribution and the additional flow at higher relative humidity is due to surface diffusion. In the narrow interval the diffusion coefficient, $D_s$ is constant and the parameter $D_{s0}$ will be revealed.

It is also possible to obtain the constant parameters of equation (13) from transient cup method measurements using the so called time-lag method. The method requires only that the functional relationship of the ingoing parameters to be known and this is provided by equation (13) that can in many cases be simplified as described in paper IV.

### 5.7 Isotopic analysis of excessive water

The objective of the study was to determine the origins of excessive water from a concrete cassette deck in an apartment building in the southern part of Sweden. The
leakage was discovered in the ceiling of one of the apartments of the building and the most plausible sources were assumed to be; surplus water from the production of the prefabricated floor elements, rainwater or possibly tap water from a broken pipeline in the building.

Isotopic analysis with a mass spectrometer revealed the $\delta$-values of the leakage water that proved to be not only different from the samples of the sources but also offset from the global meteoric line of Craig as well as the local meteoric line as given by the measurements of Calles and Westman (1989) and subsequently the water, regardless of source, must have undergone reaction since a representative value for freshwater would most reasonably have been placed on the meteoric line.

![Figure 26 Measured isotopic separation between the leakage water and the other sources (from paper III)](image)

<table>
<thead>
<tr>
<th>Source</th>
<th>$\Delta \delta^{18}O$</th>
<th>$\Delta \delta^D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water - leakage</td>
<td>-3.88</td>
<td>-15.5</td>
</tr>
<tr>
<td>Precipitation - leakage</td>
<td>-7.79</td>
<td>-40.6</td>
</tr>
<tr>
<td>Factory w. - leakage</td>
<td>-4.88</td>
<td>-21.8</td>
</tr>
</tbody>
</table>

The next step was therefore to explore whether the isotopic separation between the sample of leakage water and the other samples could be explained with any conceivable reactions. The tap water could be ruled out as a source since the isotopic separation could not be explained with any plausible reactions.

It was also highly unlikely that the leakage water had its origins in surplus water from the production of the elements since the calculated isotopic difference for the cement hardening process was much greater than the actual isotopic separation. This holds under
the assumption that the sample of water from the factory was representative for that source.

The relationship between the isotopic separation of deuterium and that of oxygen-18 suggests that the water has undergone fractionation due to evaporation. If the source of leakage was precipitation this seemed probable since considerable time had elapsed from the building of the house until the leakage was detected. Furthermore, such a process could reasonably be assumed to follow a Rayleigh-type evolution in which case the isotopic ratio of the diminishing reservoir can be calculated according to equation (27).

Figure 27 shows the calculated evolution of the abundance ratios, beginning with the values of the rainwater sample as a function of the fraction $f$, left of the reservoir.

![Graph](image)

**Figure 27** Calculated abundance ratios for evaporating rainwater following a Rayleigh evolution at 10°C as a function of the fraction left of the reservoir, $f$.

A comparison of the abundance ratios for the leakage water that are about -45.7 and -4.57 for deuterium and oxygen-18 respectively with the previous figure it is clearly possible that the leakage is rainwater that accumulated during the building period, the half of which has evaporated before seeping through the construction (which equals an $f$ value of 0.5).
5.8 Reactions and isotopic differences

In the diffusion measurements it was assumed that the reactions follow a Rayleigh-type evolution where the fractionation factor is the multiplicity of the fractionation factors for evaporation in the boxes and for diffusion through the material. The measurement results are shown in figure 28 that depicts the isotopic separation for both oxygen-18 and deuterium as a function of the fraction left of the reservoir as well as the calculated isotopic differences.

![Graph showing isotopic separation and calculated differences](image)

**Figure 28** The measured isotopic separation and the calculated isotopic differences for oxygen-18 and deuterium for a process of evaporation followed by diffusion.

The results of the study suggest that the process has been correctly modelled as a Rayleigh process of evaporation followed by diffusion.

The results of the second experiment that was carried out on the effects of sorption and capillary uptake on the isotopic content by analysis of the remaining water did not show any clear indications of the relationship between the fraction left of the reservoir and the isotopic separation or either oxygen-18 or deuterium or their ratio. It would therefore be
of interest to repeat the experiment with a greater number of samples. This will have to be the subject of future work.

6. PRACTICAL CONSEQUENCES

6.1 A moisture barrier is needed

This study shows that the moisture conditions in walls with an air barrier but open to moisture diffusion could be described with a transient diffusion model that takes into account the sorption properties of the materials.

According to the measurement results, a wall construction with loose-fill cellulose fibre insulation and no traditional vapour barrier might escape condensation and high levels of relative humidity when the moisture loads are low. When the calculation model is applied however, it can be seen that an indoor moisture production exceeding 2 g/m$^3$ will cause condensation on the inside of the external sheathing and high relative humidity in the insulation. Using the commonly recommended design value of 4 g/m$^3$ moisture will most probably cause damage to the construction since high relative humidity will coincide with the temperature required for mould growth.

6.2 Evaluation of material properties regarding moisture transport

Tracer gas measurements provide an alternative method of evaluating the water vapour permeability of porous building materials. In contrast to the cup method, the method is swift, providing results in a number of hours instead of months and economically feasible since a climatic chamber is not required.

It must be noted that the tracer gas measurements make it possible to calculate the potential transport of water vapour due to Fickian diffusion. For great many purposes that will be sufficient and fully adequate for materials the water vapour permeability of which is known to be independent of the moisture content.

There is no denying that some materials show an increase in the water vapour permeability with an increase in moisture content. This is due to surface diffusion that is
best investigated with water vapour since it depends on the interaction between the water vapour and the internal surface of the material. It has been confirmed through cup method measurements that the diffusion coefficient for the materials in question is exponentially dependent on temperature, which is something that characterises an activated process, and therefore it is natural to apply the Random Hopping Model for surface diffusion to explain the concentration dependency.

It has been explained how the constant coefficients of the Random Hopping Model can be obtained from either a number of steady state measurements or a transient measurement using the time lag method. For modelling purposes the effort of measuring the concentration dependency of the water vapour permeability might however often be superfluous.

Bearing that in mind, for most porous building materials the tracer gas method will, in a fast way, at least provide information that is far more accurate than general data from the literature.

6.3 Identification of excessive water

Isotopic analysis can be used to trace the origins of excessive water in buildings. A definite identification requires representative samples of the possible sources to be taken and that the eventual reactions are known as well as the conditions under which they took place. But even in those instances when only a sample of the excessive water can be gathered a lot of information can be gathered from the relationship to the local meteoric line for freshwater. In that case the identification process may seem more speculative but is indeed decisive enough to build a hypothesis that can be confirmed by complementary observations or at least be used to exclude some possible source from the list of candidates.

6.4 Analysis of transport processes and reactions with isotopes

The effects of several common reactions in buildings and building material on the isotopic content of water have been evaluated. It has been shown how the magnitude of
isotopic separation of oxygen-18 and deuterium and the ratio thereof varies for different reactions and transport processes. This will make it possible to determine whether a certain reaction has been involved in the history of the water, which in turn can be used to describe the physical mechanisms of transport through building materials as well as to describe the movement of water within buildings.

The work has included the development of methods for evaluating the effect of reactions on isotopic content. Some measurement results suggest that analysis of water remaining from a reaction is feasible since the method of retrieving the sample will not cause fractionation.
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